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# Predicting Surface Clustering at Ambient Conditions from Thermodynamic Data

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## Abstract

Scanning tunneling microscopy (STM) has proved to be a prime tool to characterize the atomic structure of crystal surfaces under UHV conditions. With the development of high-pressure scanning tunneling microscopy (HP-STM) the scope of this technique has been largely extended, as new structures were found to occur under gas phase chemical potentials achieved under ambient conditions. Particularly interesting is the substantial restructuring of initially flat and stable surfaces into new orientations by formation of nanoclusters. Here we discuss the possible generality of this phenomenon by analyzing cases where atomically flat surfaces of certain transition metals undergo such changes in the presence of CO at room temperature (RT) whilst some remain unchanged. From our analysis we argue that such changes can be predicted from thermodynamic data published in the literature, particularly from the difference in adsorption energy on low and high coordination sites, like terrace and step sites, which can be obtained from thermal desorption spectroscopy (TDS) measurements, and possibly also from theoretical calculations. For the vicinal surfaces with high Miller-indices, changes in the

repulsive elastic interactions between the ordered steps due to adsorbates may also play an important role.

## **1. Introduction**

### **1.1 Atomic Structure at Ambient Pressures**

Surface science is the field of elucidating the structure and fundamental physical and chemical processes occurring in a wide range of surfaces. Surface science studies provide useful information to industrial fields like heterogeneous catalysis, electrochemistry, corrosion, and lubrication. Traditional surface science is carried out at the refined conditions of ultra-high vacuum (UHV) and sometimes at cryogenic temperatures, which makes it possible to control the sample composition and cleanliness to within 0.1% of a monolayer (ML) or better, and has provided the core of our present understanding of solid surfaces.<sup>1-3</sup> An extensive array of surface-sensitive microscopy and spectroscopy techniques have revealed the atomic, electronic, and chemical structure of many crystal surfaces in their pristine clean state. Low pressure and low temperature experiments have also helped us to understand the kinetics and thermodynamics of certain model reactions, such as the one illustrated in Figure 1. However, the reactions relevant to heterogeneous catalysis typically take place in the presence of gases (or liquids) at much higher pressures and at room temperature (RT) or above, where our atomic level knowledge is far less extensive. One of the main barriers to a better understanding of the relationship between the catalyst structure and its performance has been the absence of suitable techniques that can probe surfaces in the presence of gases at the atomic scale. Over the past few decades, some of the classical surface science tools have been adapted to enable measurements at pressures closer to ambient, which has started to bridge the ‘pressure gap’ between traditional surface science and that in conditions relevant to industrial processes. High pressure scanning tunneling microscopy (HP-STM) is one of these techniques,<sup>4-6</sup> which provided atomically resolved images of surfaces in the presence of gases at RT and above. The active components of most industrial heterogeneous catalysts are based on transition metals. Therefore, most of the research so far with HPSTM has been performed on transition metal surfaces.

The electronic and chemical properties of transition metal surfaces are directly influenced by its atomic structure. Therefore, revealing the atomic structure of a metal surface is essential to obtain a fundamental understanding of the catalytic reactions occurring on it. Furthermore, that knowledge can help to explain

other important phenomena involving restructuring, such as nanoclustering, dealloying, chemical changes such as oxidation and carbidization, dense adsorbate coverage, etc. (Figure 2), which may occur with the gas phase chemical potentials prevalent under ambient conditions. The scope of this perspective article is limited to discuss the phenomenon of surface nanoclustering, i.e., the formation of small metal clusters in an initially flat low Miller-index crystal surface, and the formation of dense adsorbate layers (without surface reconstructions). Both phenomena were observed in the literature and our goal in this work is draw some guidelines on when to expect nanoclustering of transition metal surfaces. In the final section, we mention some of the latest studies on more complex materials like bimetallic surfaces, metal/oxide interfaces, and nanoparticles (NPs).

## 1.2 Thermodynamics and Kinetics

From a thermodynamic point of view, the importance of performing surface science studies at ambient pressures can be best justified by considering the change in Gibbs free energy,  $\Delta G = \theta \cdot [E_b + T\Delta S - kT \cdot \ln(p/p^0)] + 2\Delta\gamma$ , where  $\theta$  is the adsorbate coverage in monolayers,  $E_b$  is the adsorbate binding energy (i.e., adsorption energy), which is always negative,  $\Delta\mu = T\Delta S - kT \cdot \ln(p/p^0)$  is the chemical potential of the molecules in the gas phase with entropic correction, and  $\Delta\gamma$  is the surface energy.<sup>8</sup> At cryogenic temperatures and UHV,  $\Delta\mu \rightarrow 0$  so the energy minimum for an unreconstructed surface (i.e.,  $\Delta\gamma = 0$ ) occurs when  $|\theta \cdot E_b(\theta)|$  is highest. Even at low pressures (e.g., doses in the order of Langmuirs), surfaces can still reconstruct if  $|\theta \cdot E_b(\theta)| > 2\Delta\gamma$ . Under ambient conditions ( $p = 1$  bar, and  $RT = 295$  K) the ‘pressure driving force’ is roughly 0.75 eV, which together with the higher temperature relative to cryogenic conditions, lifts the kinetic limitations encountered in traditional surface science and makes surface reconstructions more likely to happen. For the simple case of adsorption of a single species onto a metallic surface, the atomic restructuring (including nanoclustering) of the surface is a matter of whether the increase in adsorbate binding energy through the formation of new low-coordinated surface sites can overcome the increase in the surface energy due the increase in the number of lower-coordination atoms. The cohesive energy of the adsorbent metal is also an important factor in the energy balance because even if surface restructuring is energetically favored, it might still not occur

at measurable rates due to kinetic limitations, i.e., high activation energy to break the chemical bonds between the surface atoms.

## **2. Discussion**

### **2.1 Case Study 1: CO on (111) Surfaces of Compact Metals**

Carbon monoxide (CO) is an extensively used probe gas in atomic scale studies of surfaces, both in UHV and at ambient pressures. Here we will compare cases where nano-structuring was observed and others where it did not occur. Two of the early studies were performed on Pt(111) and Rh(111) surfaces in the presence of up to 1 bar CO.<sup>9,10</sup> In both cases CO formed a dense adsorbate structure, as shown in the models in Figure 3. No cluster formation or other reconstructions of the surface were observed there. In contrast, the Cu(111) surface was recently shown to break up into clusters in the presence of  $\sim 0.1$  Torr CO (Figure 4).<sup>11</sup> Later it was shown that formation of clusters of Cu atoms is a general occurrence in all the low Miller-index surfaces of Cu.<sup>12,13</sup> Although at RT the Pt(111) surfaces did not reconstruct under high CO pressure, the vicinal (regularly stepped) Pt(557) and Pt(332) surfaces, which form a  $\sim 10^\circ$  angle with the (111) terraces, did reconstruct by formation of Pt clusters (Figure 5).<sup>14</sup> Interestingly the shape and symmetry of the clusters were different in the two surfaces. This is related to the different structure of the non-crossing steps in these surfaces, the Pt(557) with square (A-type), and the Pt(332) with local triangular step edge atomic structures (B-type), respectively. Both in the case of Cu(111), Pt(557), and Pt(332) surfaces, the HPSTM observations were backed up with energetic calculations within the density functional theory (DFT) framework.

An interesting question is the reason for cluster formation on Cu(111) whilst the Pt(111) and Rh(111) surfaces remained unchanged in the presence of gas phase CO at RT. Cluster formation results from the energy gain through adsorption on the newly formed low-coordinated sites (e.g., periphery atoms of the nanoclusters) exceeding the energy loss due to break of the metal-metal bonds. Therefore, it should be possible to use thermodynamics data to predict surface nanoclustering, which could be extremely helpful in the design of new experiments. For example, one could compare the CO adsorption energies at steps and terraces, obtained from thermal desorption spectroscopy (TDS) on flat and stepped surfaces, many of them

readily available in the published literature. Since the coordination number of the atoms in both A and B type of step edges of the (111) face of face-centered cubic (fcc) crystals are 7 compared to 9 of the terrace atoms, their energies can approximate those of the periphery atoms in two-dimensional clusters. Table 1 summarizes the results of TDS measurements on some of the stepped Pt, Rh, Cu, Au, and Pd surfaces with (111) terraces, as well as the cohesive energy of bulk atoms of each metal. The lower cohesive energy of soft metals, like Cu, Au, and Pd, would predict a stronger driving force for clustering at RT whereas Pt and Rh would probably require temperatures above RT for clustering to start. In terms of gain in energy, the table suggests that no clustering should be observed on Pd(111) and on Rh(111) samples, in line with observations mentioned in the previous paragraph for the Rh(111), Pt(111), and Cu(111) crystal surfaces. Using this table, we can thus predict that Au surface should be prone to breaking up into clusters in the presence of CO in the Torr-bar range at RT, whereas Pd(111) will not. Indeed, cluster formation was observed on the terraces of the Au(111) surface, already at low CO pressure, around  $1 \times 10^{-8}$  to  $1 \times 10^{-4}$  Torr (exposure in the order of  $10^6$  Langmuir) at RT. We should mention here that this is a special case: Because the Au(111) surface is already reconstructed in vacuum in the form of Au(111)- $22 \times \sqrt{3}$ , the so-called herringbone structure, the clustering was attributed to atom extraction from the steps as well as from dislocation sites of this herringbone structure.<sup>15</sup> Other low Miller-index surfaces of Pt are also special cases as they are also already reconstructed in vacuum, which makes them more prone to clustering or other type of transformation of the surface structure.<sup>4,16-17</sup>

We can also predict that for soft metals like Cu, Au, Ag, etc. nanoclustering is a likely phenomenon to happen for other gases as well. For instance, for Cu(100) it was shown that CO<sub>2</sub> also can break up the surface into nanoclusters,<sup>31</sup> whereas methanol adsorbed as a dense methoxy layer with no nanoclustering due to its adsorption energy on terraces and steps being very similar.<sup>32</sup>

## **2.2 Case Study 2: CO on vicinal Pt(111) surfaces**

Another interesting question that arises from these observations is why the Pt(111) surface does not show break-up into clusters at pressures up to 1 bar, since no surface is perfect and steps are always present, albeit with much larger (111)

terraces. Pt(997), which has terraces approximately 1.5 times larger than those of the Pt(557) and Pt(332) orientations, was shown to reconstruct under CO by step doubling,<sup>33</sup> which was also observed on the narrow terraces at lower CO pressures at around  $10^{-8}$  Torr (Figure 5b).<sup>14</sup> Clearly the different behavior between short terraces and large terraces poses an interesting and yet unresolved question. A possible explanation may lie in the strength of the repulsive interactions between non-crossing steps. Ignoring the entropic and thermal interactions at low temperatures and electronic interactions which decay exponentially with terrace width,<sup>34</sup> the parallel steps in surfaces interact electrostatically and elastically. The former is due to the electrostatic dipoles at steps, whereas the latter is caused by the atomic relaxations to minimize the electronic energy of the unsaturated (dangling) orbitals by moving closer to the second layer atoms.<sup>35,36</sup> In the specific case of stepped Pt(111) and Cu(111) surfaces, electrostatic interaction between steps is significantly lower than the elastic interaction between steps.<sup>34,35</sup> Since the dominant elastic interaction between the steps scales inversely proportional to square power of the terrace width, it might explain why steps separated by narrower terraces are more prone to reconstructions. This difference in behavior upon CO adsorption is an interesting question awaiting further theoretical investigations and experimental tests.

We would like to underline here the difference between the driving forces leading to restructuring in the form of step-doubling or step-bunching and restructuring in the form of clustering. The clustering, as we discussed before, is a consequence of the difference in adsorbate binding energies in low and high coordination sites and is expected to be more probable on metals with low cohesive energy. The stability of regularly spaced steps, on the other hand, is due to the repulsive interaction from elastic dipoles, decaying fast with distance. This can be altered by adsorbates, as the electronic landscape of the surface will change. In a very simplistic picture, CO adsorption will weaken the interaction between the first and second surface layers, so that surface atoms are pulled out and thereby repulsive interaction between the steps should be reduced.

Final remarks should be made about the nanoclustering of stepped crystal surfaces: Here the window of temperature for nanoclustering to initiate (given that it is thermodynamically favorable) is likely to happen at lower temperatures than for



the flat (111) surfaces due to lower coordination number. For instance, the cohesive energy of a Pt(111) surface atom on a step is roughly 1 eV lower than that of a surface atom on a terrace.

## 2.3 New Directions

In addition to elemental transition metal catalysts, bimetallic surfaces and oxides are worth investigating with HPSTM in the future. Similar studies can be done on NPs by using environmental transmission electron microscopy (E-TEM).

Bimetallic surfaces: There is an ongoing effort to explore bimetallic catalysts with the goal of benefiting from the desired properties of each constituent metal. Most bimetallic surfaces are yet to be studied with HPSTM because a thorough understanding of the single component metal systems should first precede it. Recipes for preparing bimetallic surfaces are available in the literature thanks to decades of surface science studies. Figure 6 represents an example from a CuCo surface alloy, which de-alloys and also breaks up into nanoclusters in the presence of CO.<sup>37</sup>

Oxides on metals: More than 90% of industrial-type catalysts are supported on oxides. These oxides are thought to have little catalytic activity by themselves, but they are not passive elements. The metal/oxide interface indeed plays an important role in catalytic processes,<sup>38</sup> a phenomenon which is still poorly understood. One way to mimic such surfaces is to use the inverse geometry, i.e., prepare thin oxide layers on metallic substrates.<sup>39</sup> Other groups have demonstrated the strength of this approach, for instance a recent study with ceria films on Cu(111) showed an enhanced activity for the methanol synthesis reaction at this interface.<sup>40</sup>

Nanoparticles: Metallic NPs supported on oxides are model systems with the closest resemblance to industrial catalysts. Despite the fact that NPs cannot be imaged with STM with atomic resolution, they can be studied with in situ TEM and with spectroscopy methods to determine changes in surface coordination number. Changes in the spectral features in CO adsorption experiments on Pd NPs pointed out to the formation of the so-called second generation NPs,<sup>41</sup> which should essentially be formed by the same driving mechanism discussed in this work. At a first glance, this contradicts with the TDS data shown in Table 1, which compares

the CO adsorption energies on 7 and 9 coordinated sites, but lowering the average coordination number increases the number of adsorption sites, and the DFT calculations support this claim.

### **3. Conclusion**

In summary, we propose that the nanostructuring of transition metal crystal surfaces in the presence of gases at RT and above can be predicted from TDS data in the literature, or from calculations if available. The lesson from the few case studies so far is that if the energy difference in adsorption between step and terrace atoms is high enough, the metal exhibits a strong potential for clustering. However, for metals with high cohesive energy, this might happen at negligible rate at RT. Further research is required to understand their behavior at higher temperatures. Vicinal surfaces are more prone to clustering than flat surfaces. The repulsive interaction between the steps in vicinal surfaces is an additional factor which affects step-doubling, step-bunching, and faceting.

### **Acknowledgements:**

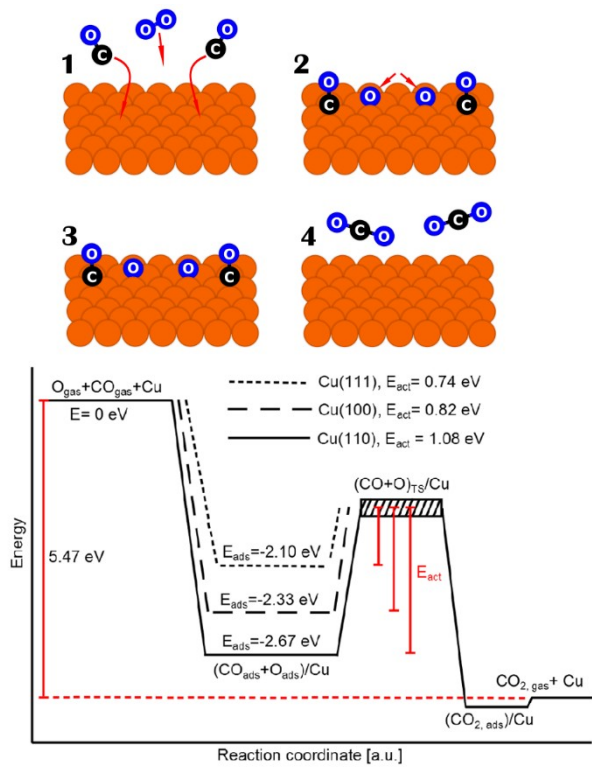
B.E. acknowledges the support from the Abramson Family Center for Young Scientists. M.S. acknowledges the support from the Office of Basic Energy Sciences (BES), Division of Materials Sciences and Engineering, of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231, through the Structure and Dynamics of Materials Interfaces (FWP KC31SM).

## Figures and Tables:

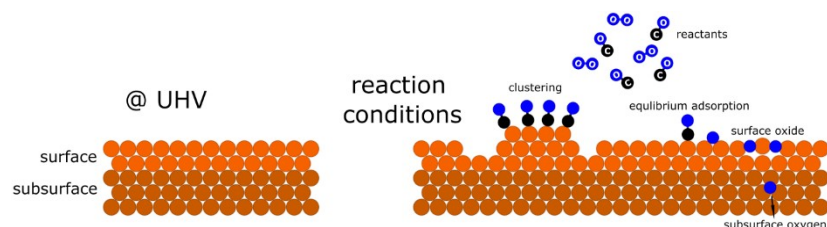
**Table 1** Desorption temperatures or adsorption energies from TDS in literature. \*No Redhead analysis<sup>18</sup> was done, only the difference in temperature is presented. \*\*Theoretical DFT study only. \*\*\*No additional desorption peak due to step edges (i.e., TDS has a single feature at low coverage) \*\*\*\*Same desorption behavior claimed for Rh(111) and Rh(331) surfaces. A type: (100) step edges, B type: (111) step edges. cov.: coverage. Bold characters indicate potential for nanocluster formation in the presence of CO.

	E <sub>b</sub> or T <sub>d</sub> @ terrace or (111) surface	E <sub>b</sub> or T <sub>d</sub> @ step	Difference	Cohesive energy (eV/atom)
Pt	460 K (low cov.) <sup>19</sup> 420 K (high cov.) <sup>19</sup> 1.19 eV (low cov.) <sup>20</sup> 1.01 eV (high cov.) <sup>20</sup> 450 K (low cov.) <sup>21</sup> 410 K (high cov.) <sup>21</sup>	540 K (B type, low cov.) <sup>19</sup> 510 K (B type, high cov.) <sup>19</sup> 1.39 eV (A type, low cov.) <sup>20</sup> 1.24 eV (A type, high cov.) <sup>20</sup> 530 K (A type, low cov.) <sup>21</sup> 510 K (A type, high cov.) <sup>21</sup>	<b>80 K*</b> <b>90 K*</b> <b>0.23 eV</b> <b>0.2 eV</b> <b>80 K*</b> <b>100 K*</b>	5.84
Au	0.17 eV <sup>24</sup> 0.28-0.39 eV <sup>25</sup>	0.5 eV (B type) <sup>22</sup>  0.47 eV (A type) <sup>24</sup> 0.52 eV (A type) <sup>25</sup>	<b>0.13 eV</b> <b>~0.3</b> <b>eV**<sup>23</sup></b> <b>0.3 eV**</b> <b>0.13-0.24</b> <b>eV</b>	<b>3.81</b>
Pd	1.47 eV (low cov.) <sup>26</sup> 1.39-1.55 eV (refs in <sup>27</sup> )	1.47 eV (B type, low cov.) <sup>26</sup> 1.48 eV (A type, low cov.) <sup>27</sup>	0 eV 0 eV***	<b>3.89</b>
Rh		(B type, low cov.) <sup>28</sup> (B type) <sup>29</sup>	0 eV*** 0 eV****	5.75
Cu	0.45-0.53 eV <sup>30</sup>	0.7 eV (B type) <sup>30</sup>	<b>0.17-0.25</b>	<b>3.49</b>

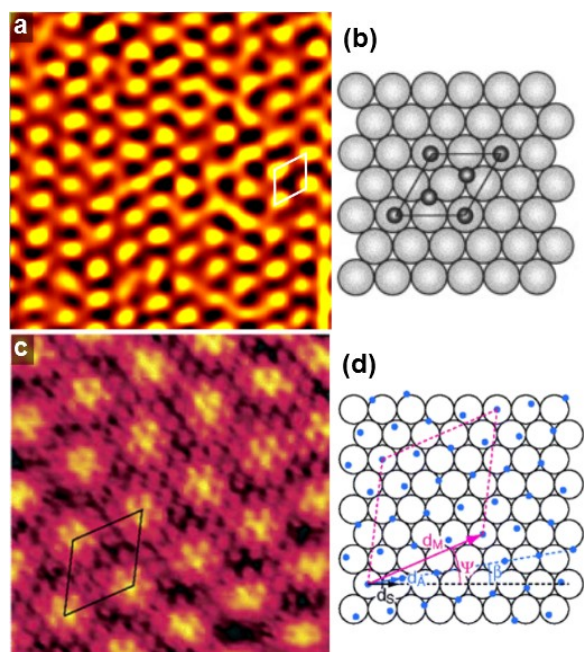
			<b>eV</b>	
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**Fig. 1** (top) Schematic representation of the catalytic CO oxidation reaction on a model Cu surface. (bottom) CO oxidation reaction on low Miller-index Cu surfaces studied with the classical surface science approach. As a result, activation energies ( $E_{\text{act}}$ ) of the reaction were obtained. On a real catalyst in the presence of gases and at elevated temperatures, however, even this simple reaction is far more complicated than this scheme represents. Bottom image is reprinted with permission from Ref.<sup>7</sup>. Copyright (2015) American Chemical Society.

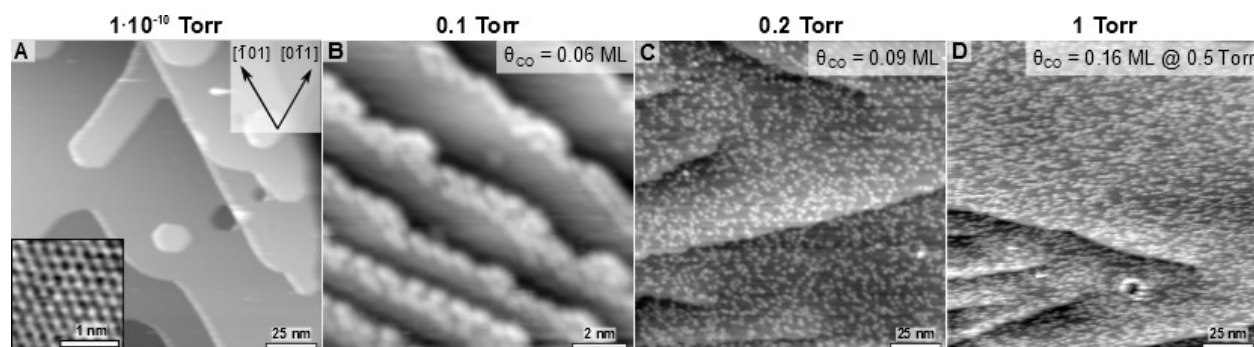


**Fig. 2** The atomically flat metallic surfaces at UHV can undergo various atomic and chemical changes in the presence of reactant gases.

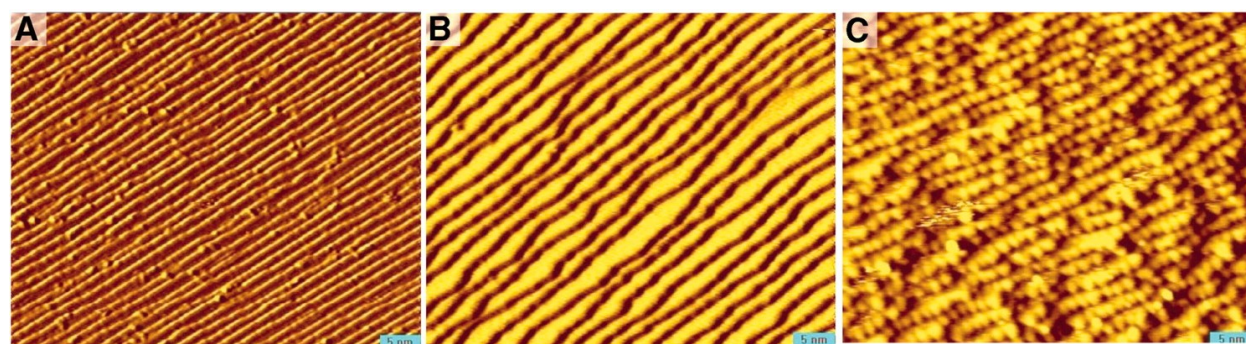


**Fig. 3** STM images of (a) Rh(111) and (c) Pt(111) surfaces at RT in the presence of 1 bar CO in the gas phase. (b) and (d) show the models predicting the adsorption sites of CO molecules in each structure with both metal surfaces remaining unchanged. (a) and (b) are reprinted with the permission from Ref.<sup>10</sup>. Copyright

(2000) Elsevier. (c) and (d) are reprinted with the permission from Ref.<sup>9</sup>. Copyright (2004) American Chemical Society.

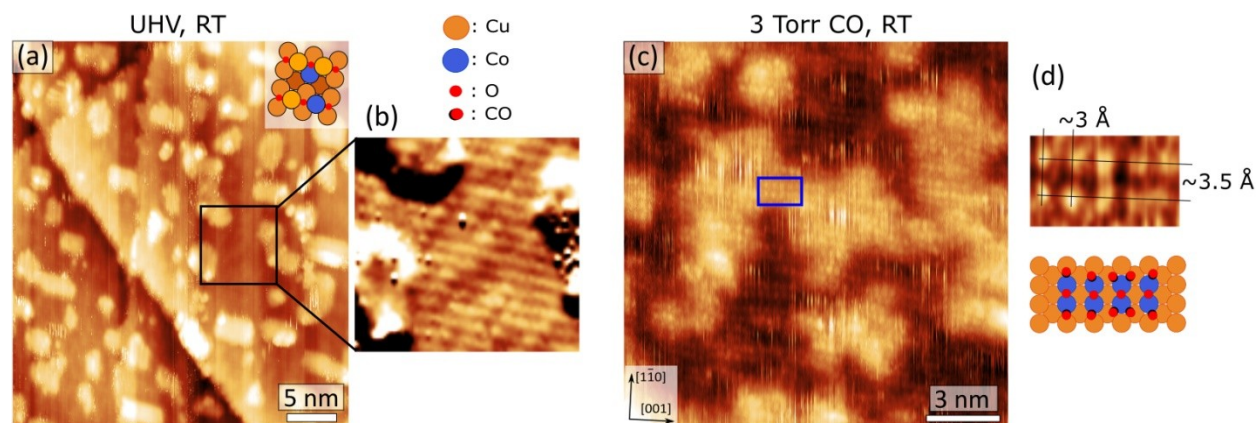


**Fig. 4** HPSTM images revealing the changes in the atomic structure of the Cu(111) surface at RT as a function of CO pressure. While terraces separated by monatomic steps are the only features at UHV (a), first the step edges (b) and then the entire surface breaks up into clusters (c) as the pressure is increased into the Torr range. The clusters increase in size and density as the pressure is further ramped up (d). The CO coverage, evaluated from spectroscopy measurements under comparable conditions, increased from 0.06 ML at 0.1 Torr to 0.09 ML at 0.2 Torr and to 0.16 ML at 0.5 Torr CO. Adapted with permission from Ref.<sup>11</sup>. Copyright (2016) American Association for the Advancement of Science.



**Fig. 5** STM images of Pt(557) (a) in UHV with a background pressure of  $1 \times 10^{-10}$  Torr; (b) under  $\sim 5 \times 10^{-8}$  Torr CO; and (c) under 1 Torr CO. (b) is an example of step-doubling. Images are  $40 \times 50 \text{ nm}^2$  in size. Reprinted with the permission from Ref.<sup>14</sup>. Copyright (2010) American Association for the Advancement of Science.





**Fig. 6** STM images of the CuCo surface (a) prior to CO dosing in UHV and (c) in the presence of 3 Torr CO at RT. (b) and (d) are the expanded area, where the suggested ball models are also shown. Before dosing CO, the surface is composed of a CuCo alloy, which de-alloys in the presence of CO at 3 Torr. In (d), the maxima are assigned to CO molecules bound to top Co sites forming dimers in short rows along the [001] direction. The expanded image in (b) is shown in the derivative mode to enhance the contrast inside the linear structures which consist of both Co and Cu atoms, with Co appearing higher due to higher electron density near the Fermi level. Adapted with permission from Ref.<sup>37</sup>. Copyright (2018) American Chemical Society.

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## TOC Graphic

